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## EUROPEAN PATENT APPLICATION

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㉚ Method of forming a glass or ceramic product.

㉛ A method of forming a glass or ceramic product is disclosed by the direct casting of a non-aqueous suspension of a particulate oxide such as fumed SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> into a final product configuration, wherein a non-aqueous oxide suspension of limited stability against gelation is cast into shape, permitted to gel, and then dried to provide an integral monolith which can be sintered or otherwise processed to clear glass or non-porous ceramic product.

EP 0 138 307 A1

-1-

METHOD OF FORMING A GLASS  
OR CERAMIC PRODUCT

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The present invention relates to the manufacture of glass or ceramic products from particulate oxides, and particularly to an improved method of making such products by the direct casting of non-aqueous suspensions.

5 It has been recognized that very pure glass and ceramic products can be made using pure fumed oxide starting materials. For example pure fused silica glasses have been used to make glass optical waveguide fibers which exhibit extremely high transparency.

10 A well known method for producing massive articles from pure fumed oxides is to deposit the oxide particles immediately after they are formed (e.g. in a flame) on a substrate or preform where they adhere to form a porous monolith. This porous body can then be 15 sintered to clear glass and, if necessary, further shaped to a limited degree to provide a product of a desired shape.

There are some shapes which cannot conveniently be formed by the direct deposition of the oxides onto a 20 preform. Accordingly, efforts have been made to develop other ways to process these oxides. However, fumed oxides are generally fluffy, high-surface-area materials (surface areas typically range from 25-400  $\text{m}^2/\text{gram}$ , with average particle sizes typically in the 25 range from 0.01-0.5 microns), and they are very difficult to process by slip-casting or other methods conveniently used for shaping ceramic starting materials.

US Patents Nos. 4,042,361 and 4,200,445 disclose 30 one approach to the problem which involves dispersing the fumed oxides in water to form a suspension. This suspension is then processed by casting into thin sheets,

drying to cause fragmentation or dicing into porous granules, sintering the porous granules to form a densified granular material, milling the densified material to form a casting slip, and finally casting 5 the slip to form a green ceramic shape which can be fired to provide a glass product.

The process disclosed in the above two patents disadvantageously requires the handling of aqueous suspensions of fumed oxides which do not exhibit long shelf 10 life and are relatively viscous even at moderate oxide concentrations. In addition, massive articles are not readily cast directly from aqueous suspensions, due to cracking problems. Thus, according to the above patents, a relatively large number of process steps are required 15 before the final cast shape is obtained.

It has recently been proposed in European Patent Application No. 83306204.5 to use non-aqueous dispersions of particulate oxidic materials such as fumed oxides to form glass articles by direct casting into final shape. 20 In this process the cast shape is formed not by slip casting but by gelation of the suspension in its final configuration, followed by removal of the vehicle and sintering of the resulting porous monolith. This method avoids the intermediate dicing and calcining 25 steps required with water suspensions, and the non-aqueous oxide suspensions used are generally stable and easy to cast.

In the process of the above-described patent application the suspensions are generally stable against 30 gelation and accordingly added gelling agents are used to cause rapid conversion of the fluid suspension to a semi-rigid gelled shape. However, there are some applications for which such rapid gelation is not required, and wherein gelling intervals of the order of 24-48 hours 35 would be adequate. Further, applications exist wherein

the use of added gelling agents would be an unnecessary or even an undesirable expedient, from either a processing or chemical composition standpoint.

In accordance with the present invention the use  
5 of a gelling agent is avoided by preparing a non-aqueous suspension of particulate oxidic material which is of only limited stability. In accordance with prior practice, the general process steps are to prepare a fluid suspension of the oxide in a non-aqueous vehicle,  
10 cast the suspension to the final product configuration, permit the suspension to gel in that configuration, and remove the vehicle from the gelled casting to provide a porous monolith. Generally, no change in cast configuration except for shrinkage due to drying will occur.

15 In accordance with the present invention, however, rather than preparing a fully stable suspension which requires an added gelling agent to promote gelation, a suspension is prepared which contains an amount of an added dispersant effective only to obtain a suspension  
20 of limited stability. The amount used is sufficient to permit effective dispersion of the oxide in the non-aqueous vehicle, but ineffective to delay gelation of the suspension for a period longer than about 48 hours from the time of dispersion. A suspension prepared in  
25 this way is fluid and can be cast into any desired shape within a useful interval after dispersion. However, it will automatically gel within a period of hours after casting so that the vehicle can be efficiently removed from the gelled shape, without cracking of the casting,  
30 prior to sintering or other processing of the cast shape.

Particulate oxidic materials amenable to processing in accordance with the invention include any of the fumed oxides produced by the known flame oxidation or flame hydrolysis processes, including  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  
35  $\text{ZrO}_2$ ,  $\text{SnO}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{GeO}_2$  and  $\text{B}_2\text{O}_3$  and the like. These

processes produce oxide particle sizes below 1 micron and typically in the range of about 0.01-0.5 microns which are quite suitable for handling in accordance with the invention. In addition to pure fumed oxides and mixtures of these oxides it is possible to use oxidic materials of appropriate particle size produced by other processes, as well as multicomponent oxide materials produced by the flame oxidation of mixtures of precursor materials. These include  $\text{SiO}_2\text{-B}_2\text{O}_3$ ,  $\text{SiO}_2\text{-}$

5  $\text{GeO}_2$ ,  $\text{SiO}_2\text{-P}_2\text{O}_5$  and similar compositions which may produce amorphous (non-crystalline or glassy) fumed oxide particles, also known as soot, upon flame oxidation. Hence crystalline or non-crystalline oxide materials produced by any suitable process can be used.

10 15 It is desirable prior to incorporation of a fumed or other oxide into the vehicle to dry the oxide to remove adsorbed water from the particles. The presence of water can cause undesirable gelling of these suspensions. Typically, heating the oxide material above

20 25 about 100°C in air or other dry environment for a short interval prior to use is sufficient.

Non-aqueous vehicles which can be used in accordance with the invention include n-hexane, chloroform, methylene chloride, methanol, ethanol, and other low-molecular weight unsubstituted or OH- or halogen-substituted hydrocarbons of similar character. Water is not a suitable vehicle because it is not a medium in which fumed oxides are easily dispersed, and because castings containing a water vehicle are prone to crack-

30 35 ing during the vehicle removal or drying stage of the process. Other vehicles such as 1-propanol may not be suitable if they provide a stable suspension of fumed oxides without the use of a dispersant, because such a suspension will not gel after casting. Hence vehicles which require the use of a dispersant to achieve a

0138307

-5-

flowable suspension which resists gelation to at least some degree should be used.

5 Dispersants suitable for use in accordance with  
the invention to achieve suspensions of limited stability include those effective to disperse inorganic materials  
in organic media by steric hindrance, electrical double layer, and/or polar screening mechanisms. The use of  
a steric hindrance mechanism, involving the use of a  
chain-like molecule comprising both hydrophilic and  
10 hydrophobic groups compatible respectively with the hydrophilic oxide and non-aqueous vehicle constituents of the system, is advantageous because relatively concentrated dispersions can be formed by this method.

Examples of dispersants effective to promote dispersion by steric hindrance include stearic acid, stearic alcohol, and the straight-chain lower alcohols containing 3-10 carbon atoms, e.g. n-propanol.

The technique of forming the dispersion is not critical, and the amount of dispersant effective to obtain limited stability in any particular suspension can readily be determined by routine experiment. A suitable approach is to prepare a series of vehicle mixtures containing a selected vehicle and a range of added dispersant concentrations, combine the vehicle mixtures with selected quantities of the selected oxide material to be processed, and then to determine gelling time as a function of dispersant concentration in the series under evaluation.

The invention may be further understood by reference  
35 to the following illustrative Example.

### EXAMPLE

A vehicle mixture for an oxide suspension is prepared with consists of about 150 ml. of methanol as the vehicle component and 2.2 ml. of 1-propanol as the dispersant.

35 To this vehicle is added a fumed oxide component consisting of 60 grams of fumed  $\text{SiO}_2$  produced by flame oxidation.

-6-

This oxide had been fired to 800°C in N<sub>2</sub> to remove adsorbed gases and reduce the number of silanol groups. Prior to incorporation in the suspension, it is dried at 200°C for 1 hour in a vacuum to remove adsorbed water 5 picked up in storage.

The fumed oxide is dispersed in the vehicle mixture by ball-milling the two together for about 16 hours. This suspension is then cast into a rectangular mold about 5 cm. X 7.6 cm. in size to a depth of about 10 2.5 cm, and the casting is covered with polyethylene film to prevent vehicle loss prior to gelation.

Gelation of the casting thus provided occurs within about 24 hours, after which the plastic covering film is vented to permit evaporation of the vehicle and 15 dispersant. The casting can be completely dried, with some shrinkage but without cracking, in about 3 weeks, after which it can be fired to produce an optically clear glass slab about 3.8 X 4.5 X .8 cm. in size.

While the preceding example is based on the use of 20 a methanol vehicle and a 1-propanol dispersant, 1-decanol can also be successfully used as a dispersant in this vehicle. A further example of a desirable vehicle/dispersant system is a chloroform vehicle containing a 1-propanol dispersant.

25 It is anticipated that any of the other non-aqueous vehicles hereinabove described can be used with any of the described dispersants to produce a non-aqueous fumed oxide suspension suitable for use in the invention, provided only that the amount of dispersant 30 employed is limited to that effective to permit dispersion without full stabilization of the dispersion against gelation.

## CLAIMS:

1. A method of forming a glass or ceramic product by the direct casting of a particulate oxide suspension, wherein a fluid suspension of the at least one particulate oxide in a non-aqueous vehicle is cast into a final configuration for the product, gelled in that configuration, and finally dried with no change in configuration except for shrinkage, characterized in that the suspension includes at least one dispersing agent, and in that the amount of dispersing agent present is insufficient to delay gelation of the suspension for a period longer than about 48 hours.
2. A method according to Claim 1, wherein the particulate oxide is at least one oxide selected from  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{SnO}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{GeO}_2$  and  $\text{B}_2\text{O}_3$ .
3. A method according to Claim 1, wherein the particulate oxide is a multicomponent oxide selected from  $\text{SiO}_2\text{-B}_2\text{O}_3$ ,  $\text{SiO}_2\text{-GeO}_2$  and  $\text{SiO}_2\text{-P}_2\text{O}_5$ .
4. A method according to any of claims 1 to 3, wherein the non-aqueous vehicle is methanol or chloroform.
5. A method according to any of Claims 1 to 4, wherein the dispersing agent is stearic acid or stearic alcohol.
6. A method according to any of Claims 1 to 4, wherein the dispersing agent is a normal alcohol containing 3-10 carbon atoms.



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## EUROPEAN SEARCH REPORT

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Application number

| DOCUMENTS CONSIDERED TO BE RELEVANT  |   |                              | EP 84305030.3  |
|--|---|------------------------------|--|
| Category   | Citation of document with indication, where appropriate, of relevant passages   | Relevant to claim            | CLASSIFICATION OF THE APPLICATION (Int. Cl.4)  |
| X  | <p>PATENT ABSTRACTS OF JAPAN, unexamined applications, C field, vol. 4, no. 113, August 13, 1980</p> <p>THE PATENT OFFICE JAPANESE GOVERNMENT page 73 C 21</p> <p>* Koaki-no. 55-71 637 (HITACHI) *</p> <p>--</p> | 1-4                          | C 03 B 8/02<br>C 04 B 35/00<br>C 01 B 33/145<br>C 03 C 3/00  |
| X,D  | <p><u>US - A - 4 200 445 (BIHUNIAK)</u></p> <p>* Column 3, lines 14-19, 47-53; column 8, lines 27-54 *</p> <p>--</p>  | 1-4                          |  |
| A  | <p><u>GB - A - 2 103 202 (WESTERN ELECTRIC COMPANY)</u></p> <p>* Page 1, lines 70-76, 95-99; page 2, lines 57-63; page 3, lines 21-36, 121-126; page 4, lines 1-14 *</p> <p>----</p>                              | 1-3                          | <p>TECHNICAL FIELDS<br/>SEARCHED (Int. Cl.4)</p> <p>C 03 B<br/> C 03 C<br/> C 04 B<br/> D 01 F<br/> C 01 B</p> |
| The present search report has been drawn up for all claims                       |   |                              |  |
| Place of search<br><b>VIENNA</b>   | Date of completion of the search<br><b>25-10-1984</b>   | Examiner<br><b>HAUSWIRTH</b> |  |
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